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## Reduction and selective oxo group silylation of the uranyl dication\*\*

Polly L. Arnold,<sup>1,\*</sup> Dipti Patel,<sup>1</sup> Claire Wilson<sup>2</sup> and Jason B. Love<sup>1,\*</sup>

<sup>[1]</sup>EaStCHEM, School of Chemistry, Joseph Black Building, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, UK.

<sup>[2]</sup>Rigaku Europe, Chaucer Business Park, Watery Lane, Sevenoaks, Kent TN15 6QY, UK.

<sup>[\*]</sup>Correspondence and requests for materials should be addressed to P.L.A. or J.B.L. ([polly.arnold@ed.ac.uk](mailto:polly.arnold@ed.ac.uk), [jason.love@ed.ac.uk](mailto:jason.love@ed.ac.uk)). X-ray crystallographic coordinates for **3** and **5** have been deposited at the Cambridge Crystallographic Database, numbers 649987 and 649988 respectively.

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Supplementary Information is linked to the online version of the paper at [www.nature.com/nature](http://www.nature.com/nature)

### Author contributions:

D.P. synthesized and characterized the compounds, and solved the crystal structure data. C.W. mounted the crystals, collected the single-crystal X-ray crystallographic data, modelled the disorder components in the structures, and checked the final structure solutions. P.L.A. and J.B.L. generated and managed the project, helped characterize the complexes, analysed the data and wrote the manuscript.

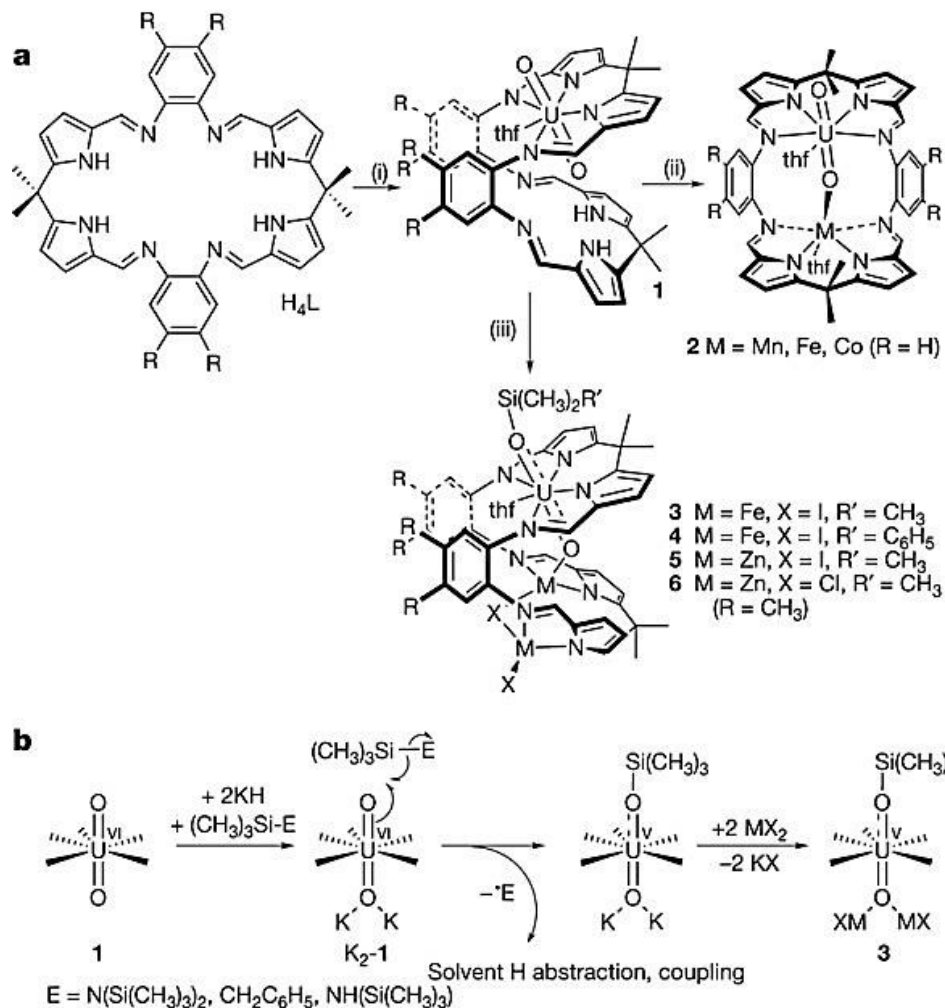
## Abstract

The uranyl dication,  $[\text{UO}_2]^{2+}$ , is the most prevalent form of uranium and is a soluble and problematic environmental contaminant<sup>1-3</sup>. Due to the mutually-strengthening, strongly covalent *trans*- $\text{UO}_2$  bonding<sup>4</sup>, it is also extraordinarily chemically robust and shows little propensity to participate in the myriad of oxo-group and redox reactions that are characteristic of  $[\text{CrO}_2]^{2+}$ ,  $[\text{MoO}_2]^{2+}$ , and other transition metal analogues<sup>5-9</sup>. As a result, there are few examples in which the oxo-groups of  $[\text{UO}_2]^{2+}$  are functionalised, and, despite the importance of reductive protonolysis reactions of the  $[\text{UO}_2]^{2+}$  cation to its precipitation from the environment, the isolation and characterisation of the singly-reduced, pentavalent uranyl cation  $[\text{UO}_2]^+$  has only recently been reported<sup>10-12</sup>. Here we show that manipulation of the uranyl dication within a rigid and well-defined molecular framework facilitates a new reaction in which both single-electron reduction, and, significantly, selective covalent bond formation at one U oxo group occurs to form an isolable, pentavalent, monofunctionalised  $[\text{O}=\text{U}^{\text{III}}\text{OR}]^+$  cation. These results demonstrate that the uranyl oxo group undergoes radical reactions that are commonly only associated with transition metal oxo groups, and provide new insight into the chemical relationships between transition metal and actinide oxo compounds. Also, in an anaerobic environment, the pentavalent uranyl cation can be straightforwardly accessed, isolated in the presence of transition metal cations, and desymmetrised. It is anticipated that these results will also provide a basis upon which to build models to help understand the chemistry of the related, but highly radioactive, plutonyl and neptunyl analogues found in nuclear waste.

## Main text

Reactions of the uranyl dication that result in the functionalization or transformation of the  $\text{U}=\text{O}$  groups are rare. Examples include atypical Lewis base behaviour of the uranyl dioxo group towards alkali metals in the solid state<sup>13, 14</sup>, and the formation of an unusual  $\text{O}=\text{U}=\text{O} \rightarrow \text{B}(\text{C}_6\text{F}_5)_3$  adduct involving significant and asymmetric  $\text{U}=\text{O}$  bond lengthening<sup>15</sup>. Photolysis of uranyl phosphine oxide complexes in the presence of alcohols results in two-electron reduction and the formation of U(IV) alkoxides, via the highly oxidizing  $^*\text{UO}_2^{2+}$  excited state; the U(IV) complexes can be hydrolysed to regenerate the uranyl dication cleanly<sup>16</sup>. Usually, the  $[\text{UO}_2]^+$  cation spontaneously disproportionates to  $[\text{UO}_2]^{2+}$  and U(IV) phases in an aqueous environment. We reported recently<sup>17</sup> that the reaction between the mono-uranyl complex, **1** ( $\text{R} = \text{H}$ ), and transition metal silylamides  $[\text{M}\{\text{N}(\text{Si}(\text{CH}_3)_3)_2\}_2]$  ( $\text{M} = \text{Mn}, \text{Fe}, \text{Co}$ ) forms the molecular cation–cation complexes, **2**, in which, uniquely, the transition metal bonds to the *endo*-uranyl oxygen atom (Fig. 1a), that is, the uranyl acts as a Lewis base to the transition metal<sup>18</sup>; in this case, no electron transfer between the metals was seen. In search of alternative synthetic routes, we have found that the one-pot reaction between **1** ( $\text{R} = \text{CH}_3$ ),  $\text{FeI}_2$ , and the silylamide base  $\text{KN}(\text{Si}(\text{CH}_3)_3)_2$  at  $-78^\circ\text{C}$  resulted in the formation of the new cation–

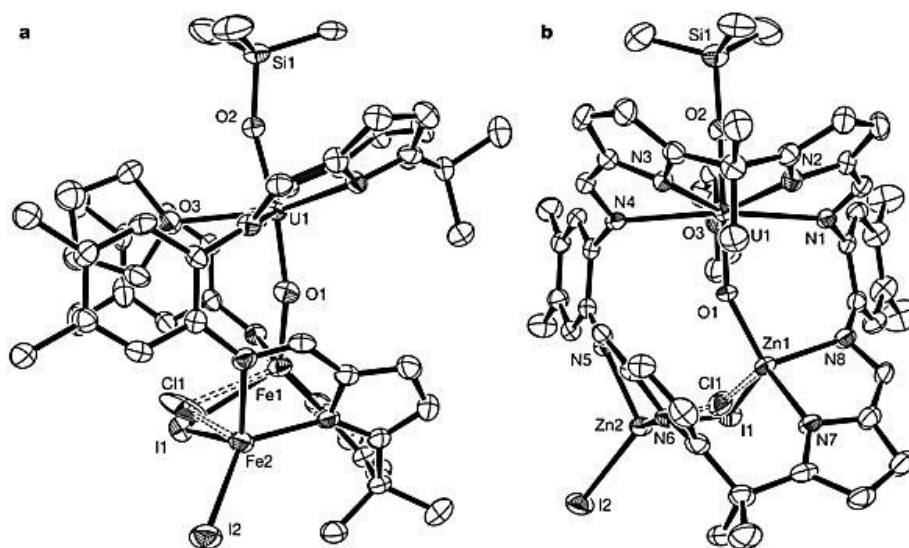
cation complex  $[\text{UO}(\text{OSi}(\text{CH}_3)_3)(\text{thf})\text{Fe}_2\text{I}_2(\text{L})]$ , **3**, in 80% isolated yield, Fig. 1a (see Methods and Supplementary Information for synthetic details; thf stands for tetrahydrofuran).



**Figure 1. (a) The synthesis of the uranyl complex **1** and cation-cation complexes. (b) the proposed mechanism of reductive silylation of the uranyl group.** Reagents and conditions (i)  $[\text{UO}_2(\text{thf})_2\{\text{N}(\text{SiMe}_3)_2\}_2]$ , thf; (ii)  $[\text{M}\{\text{N}(\text{SiMe}_3)_2\}_2]$ , thf, heat ( $\text{M} = \text{Mn, Fe, Co}$ ;  $\text{R} = \text{H}$ ); (iii) either  $\text{KN}(\text{SiMe}_2\text{R})_2$ ,  $\text{MX}_2$  ( $\text{M} = \text{Fe}$ ,  $\text{X} = \text{I}$ ,  $\text{R}' = \text{Me, Ph}$ ;  $\text{M} = \text{Zn}$ ,  $\text{X} = \text{Cl, I}$ ,  $\text{R}' = \text{Me}$ ); or  $\text{KH}$ ,  $\text{FeI}_2$ ,  $\text{N}(\text{SiMe}_3)_3$  or  $\text{PhCH}_2\text{SiMe}_3$ , thf,  $-80^\circ\text{C}$ .  $\text{R} = \text{Me}$ .

The X-ray single-crystal structure of **3** (Fig. 2a, and Supplementary Information) shows that the macrocycle geometry remains wedge-shaped, even though two tetrahedral Fe cations are now incorporated in the lower cavity, and a  $\text{Si}(\text{CH}_3)_3$  group is bound to the *exo*-uranyl oxygen. The uranyl cation displays a distorted pentagonal bipyramidal geometry with a linear  $\text{O1-U1-O2}$  group ( $172.16(17)^\circ$ ). The U–O bond distances confirm that the uranyl fragment in **3** is in the pentavalent oxidation state. The *endo*-U1–O1 ( $1.870(4)$  Å) bond

distance in **3** is elongated compared with those of the hexavalent  $[\text{UO}_2]^{2+}$  complexes **1** (R = H: U1–O1 1.790(4) Å) and **2** (M = Mn: U1–O1 1.808(4) Å), and is similar to experimental<sup>10, 11, 12, 19</sup> and calculated<sup>20, 21</sup> bond distances for pentavalent  $[\text{UO}_2]^+$  (range 1.811 to 1.934 Å). The *exo*-U1–O2 (1.993(4) Å) bond distance is appreciably longer than U1–O1 (compare with **2** (M = Mn): U1–O2 1.768(5) Å), but is significantly shorter than in tetravalent U–OSiR<sub>3</sub> complexes<sup>22</sup> and pentavalent U–OR compounds<sup>23</sup> (all greater than 2.0 Å). This implies that the *exo*-U–O bond still retains some multiple bond character, but less than that of the *endo*-U–O bond. Both Fe1 and Fe2 are four-coordinate and bound to the macrocycle by single iminopyrrolides, and to each other by a bridging iodide (Fe1–I1 2.7317(13) Å, Fe2–I1 2.6335(13) Å, Fe1–I1–Fe2 70.30(3)°). Notably, Fe1 bonds to the *endo*-uranyl oxygen (Fe1–O1 1.946(4) Å) at a distance commensurate with a single dative bond. The Fe-bridging iodide refined to 79.7(3)% occupancy; after exploration of a number of alternative models the remaining electron density was best modelled as a bridging chloride, considering both the quality of the refinement and comparison of the resulting geometry with literature values. The chloride contaminant has accumulated in the crystal, and derives from amounts present in the original  $[\text{UO}_2(\text{thf})_2\{\text{N}(\text{Si}(\text{CH}_3)_3)_2\}_2]$  starting material.



**Figure 2. Molecular structures of (a)  $[\text{UO}(\text{OSiMe}_3)(\text{thf})\text{Fe}_2\text{I}_2(\text{L})]$  **3**, side-on, and (b)  $[\text{UO}(\text{OSiMe}_3)(\text{thf})\text{Zn}_2\text{I}_2(\text{L})]$  **5**, face-on.** Thermal ellipsoid plot (50% probability displacement) views of (a) **3** and (b) **5**. For clarity, all hydrogen atoms and the minor thf component have been removed.

We carried out experiments to probe the origin of the  $\text{Si}(\text{CH}_3)_3$  group and to confirm the single electron transfer to form pentavalent uranyl. A mixture of **1**,  $\text{FeI}_2$ , and the phenyl-substituted  $\text{KN}(\text{Si}(\text{CH}_3)_2\text{C}_6\text{H}_5)_2$  reacts to afford the phenylsilyl-functionalized  $[\text{UO}(\text{OSi}(\text{CH}_3)_2\text{C}_6\text{H}_5)(\text{thf})\text{Fe}_2\text{I}_2(\text{L})]$  **4**, in high yield (see Supplementary Information). Thus, it is clear that the silyl group originates from either the silylamide base,

KN(Si(CH<sub>3</sub>)<sub>2</sub>R')<sub>2</sub>, or its by-product, the disilazane HN(Si(CH<sub>3</sub>)<sub>2</sub>R')<sub>2</sub> (R' = CH<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>). Analysis of the mass balance for the by-product KI shows that two molar equivalents are formed during the reaction, which implies that electron transfer from KN(Si(CH<sub>3</sub>)<sub>2</sub>R')<sub>2</sub> does not occur; that is, the silylamide acts solely as a base, and the HN(Si(CH<sub>3</sub>)<sub>2</sub>R')<sub>2</sub> by-product formed during the reaction provides the silyl group. In contrast, chemical analogues from the same group as uranium, the molybdenum and tungsten *cis*-dioxo complexes [M<sup>VI</sup>O<sub>2</sub>(L')<sub>2</sub>]<sup>2-</sup> (M = Mo, W; L' = 1,2-S<sub>2</sub>C<sub>6</sub>H<sub>4</sub>), are readily silylated, even in the absence of redox reactions, to afford [M<sup>VI</sup>O(OSi(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>(C<sub>4</sub>H<sub>9</sub>)<sup>t</sup>)(L')<sub>2</sub>]<sup>-</sup>. Furthermore, the silylated Mo compound is rapidly hydrolysed to the Mo(IV) mono-oxo compound [Mo<sup>IV</sup>O(L')<sub>2</sub>]<sup>2-</sup> (refs24,25).

The isolation of the closed-shell Zn(II) compounds **5** and **6** confirms that the transition metal simply stabilizes the pentavalent [UO(OSi(CH<sub>3</sub>)<sub>2</sub>R')]<sup>+</sup> fragment, without participating in redox chemistry. Reaction between **1**, KN(Si(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub>, and ZnX<sub>2</sub> (X = Cl, I) resulted in the formation of orange/brown [UO(OSi(CH<sub>3</sub>)<sub>3</sub>)(thf)Zn<sub>2</sub>X<sub>2</sub>(L)], (X = I; **5**, Cl; **6**), in moderate yields, Fig. 1a (see online Methods and Supplementary Information). The X-ray crystal structure of **5** (Fig. 2b, and Supplementary Information) is similar to that of **3**, again with trace chloride incorporated but in this case with an occupancy of 52.7(3)%. The U··O bond distances in **5** (U1–O1 1.867(3) Å, U1–O2 1.975(3) Å) are similar to those in **3**, and are also consistent with pentavalent uranyl. The U=O asymmetric stretch in the infrared spectra of uranyl compounds is normally diagnostic, and should decrease by 100–180 cm<sup>-1</sup> on reduction to [UO<sub>2</sub>]<sup>+</sup> (ref. 12). However, the infrared spectra of pentavalent **3** to **6** are complex in the fingerprint region and the expected U=O absorption features between 800–700 cm<sup>-1</sup> are masked by those of the macrocyclic ligand and the O–SiR<sub>3</sub> groups (Supplementary Fig. 1).

We have sought to generalize the reaction further, and have found that the potassium silylamide may be replaced by potassium hydride, another strong base, in combination with other sources of silyl group. Thus, the replacement of KN(Si(CH<sub>3</sub>)<sub>3</sub>)<sub>2</sub> by KH and either N(Si(CH<sub>3</sub>)<sub>3</sub>)<sub>3</sub> or C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub> is equally effective in the synthesis of **3**, affording isolated yields of up to 85%, via N–Si or C–Si bond cleavage (see online Methods). In contrast, however, treatment of **1** with a reductant (rather than a base), and a source of Si(CH<sub>3</sub>)<sub>3</sub>, in these cases cobaltocene and trimethylsilyl triflate, does not result in reductive silylation.

These data suggest that this new and general reaction to reductively silylate the uranyl oxo group requires the deprotonation of the empty macrocyclic cavity by the potassium base to form potentially an oxidizing, U(VI) intermediate **K<sub>2</sub>-1** (Fig. 1b) in which the *endo*-U=O bond is coordinated by two K cations, and the *exo*-U=O bond is now polarized sufficiently to engage in N–Si and C–Si bond cleavage.

Transition metal oxo bonds are weakened when a strong ligand is in the *trans*position (the *trans* influence). In contrast, in uranyl compounds, covalent interactions between the oxo ligands and the metal *f* orbitals mutually strengthen the two *trans* U=O bonds, the inverse *trans* influence<sup>26</sup>. In high-oxidation-state porphyrin-based iron oxo chemistry, tuning the axial ligand markedly alters the reactivity of the electrophilic Fe = O group

towards alkane hydroxylation and olefin epoxidation<sup>6</sup>. Likewise, by manipulating the uranyl oxo within the molecular cleft, we have significantly disrupted the overall UO<sub>2</sub> bonding to activate the *exo* oxo group towards reductive silylation. The ready formation of strong O–Si bonds in **3** to **6** parallels that seen in transition metal oxo chemistry in which hydrogen atom abstraction reactions do not require metal-based radicals, but instead depend on the strength of the bond between the oxidant and the hydrogen atom<sup>9</sup>. Unfortunately, attempts to isolate the proposed **K<sub>2</sub>-1** intermediate have been unsuccessful. Thermally stable, pentavalent, functionalized uranyl complexes are most readily isolated by substitution of the two K cations by transition metal halides in a reaction that eliminates KI and forms **3** to **6**. The reaction to afford **3** is equally successful when carried out in the dark, confirming the absence of any photochemically derived reactivity.

We recorded variable temperature magnetic measurements to compare the  $f^1 d^6 d^6$  UFe<sub>2</sub> system **3** with the  $f^1 d^{10} d^{10}$  UZn<sub>2</sub> system **5**. The room-temperature moment of 7.74 BM for **3** (BM = Bohr magnetons), and the Curie–Weiss behaviour (2 to 300 K) suggests the presence of two, high-spin, Fe(II) centres and one  $f^1$  U(V) centre (Supplementary Fig. 2) that are magnetically independent; the thermal variation of the product of molar magnetic susceptibility and temperature,  $\chi_M T$ , is dominated by the magnetic contribution from the Fe ions. In contrast, the magnetic behaviour for **5** (2 to 300 K) should only contain contributions from the U centre<sup>27</sup>; it displays two distinct regions (Supplementary Fig. 2) associated with the depopulation of excited crystal field states of the U(V)  $f^1$  cation and is similar to that observed for the few known organometallic pentavalent uranium complexes<sup>28, 29</sup>. The moment at low temperature rises from 0.41 to 1.11 BM and increases to 2.38 BM at high temperature. In contrast, the moment of a U(IV) ( $f^2$ ) system would be expected to be higher at room temperature (3.58 BM), and the reciprocal susceptibility would become temperature-independent below about 40 K. A preliminary electron paramagnetic resonance study of **5** in frozen methyl-thf at 5 K (Supplementary Fig. 3) displays a strong, broad resonance at  $g = 2.2$  that supports the presence of a single  $f$  electron.

We have shown that the use of a macrocyclic architecture to place the uranyl ion in a rigid and asymmetric coordination environment allows the generation of a reactive and highly oxidizing uranyl complex which can selectively cleave N–Si and C–Si bonds to form singly, covalently functionalized pentavalent uranyl complexes. These reactive U oxo compounds may also provide functional chemical models for the highly radioactive  $f^1$  plutonium and neptunium dioxo cations<sup>30</sup>.

## Methods summary

Working under a dry, oxygen-free dinitrogen atmosphere, with reagents dissolved or suspended in aprotic solvents, and combined or isolated using cannula and glove box techniques, we first treated the free macrocycle H<sub>4</sub>L with a bis(amido)uranyl precursor, to form the hinged macrocyclic complex [UO<sub>2</sub>(thf)(H<sub>2</sub>L)] in which one N<sub>4</sub>-donor compartment remains vacant. Treatment of this complex with two equivalents of

potassium base and a suitable silylated reagent (or a base containing an ancillary silyl group) afforded a soluble complex in which the uranium was shown to be both singly reduced and silylated at the *exo* oxo group, as the  $\text{UO}(\text{OSiR}_3)$  dication. This asymmetric pentavalent uranyl complex is then readily isolated, purified, and characterized by a final salt elimination reaction to produce two equivalents of potassium halide, and to place two transition metal cations (as Fe or Zn chloride or iodide salts, MX) into the remaining cavity of the macrocycle, affording  $[\text{UO}(\text{OSiR}_3)(\text{thf})(\text{L})(\text{MX})_2]$ . We characterized all compounds by elemental analysis, Fourier transform infrared spectroscopy, and either variable-temperature magnetic moment measurements or nuclear magnetic resonance (NMR) spectroscopy (paramagnetic and diamagnetic compounds respectively). Additionally, we determined the solid-state structures of two of the silylated complexes by single-crystal X-ray diffraction studies.

## Methods

**$[\text{UO}_2(\text{thf})(\text{H}_2\text{L})]\cdot\text{thf}$ , **1**** - To a stirred solution of  $[\text{UO}_2(\text{thf})_2\{\text{N}(\text{SiMe}_3)_2\}_2]$  (2.94 g, 4.0 mmol) in thf (20 mL, -78 °C) was added slowly a solution of  $\text{H}_4\text{L}$  (2.64 g, 4.0 mmol) in thf (20 mL, -78 °C). The resulting solution was allowed to warm to room temperature over 16 hours, after which the volatiles were removed under vacuum and the residual solids redissolved in thf (15 mL). Addition of hexane (20 mL) afforded a precipitate that was isolated by filtration, washed with hexane ( $2 \times 10$  mL), and dried under vacuum to yield 3.76 g, 88 % of **1** as a brown solid. Analysis. Found: C, 56.00; H, 5.55; N, 10.51.  $\text{C}_{50}\text{H}_{58}\text{N}_8\text{O}_4\text{U}$  requires: C, 55.96; H, 5.46; N, 10.44 %; IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu$  908(s) ( $\text{UO}_2$  asymmetric stretch).

**$[\text{UO}(\text{OSiMe}_3)(\text{thf})\text{Fe}_2\text{I}_2(\text{L})]$ , **3**** - To a stirred mixture of **1** (0.27 g, 0.25 mmol) and  $\text{KN}(\text{SiMe}_3)_2$  (0.10 g, 0.53 mmol) was added thf (20 mL) at -78 °C, and the resulting solution added dropwise to stirred slurry of  $\text{FeI}_2$  (0.15 g, 0.50 mmol, beads) in thf (10 mL, -78 °C). The resulting mixture was allowed to warm to room temperature over 42 hours, after which the solid KI was removed by filtration and washed with thf ( $2 \times 5$  mL). The combined filtrates were evaporated to dryness, the residual solids extracted into hot toluene (20 mL), filtered and dried under vacuum to yield 0.13 g, 81 % of **3** as a brown solid. **Analysis.** Found: C, 40.93; H, 4.07; N, 7.64.  $\text{C}_{49}\text{H}_{57}\text{N}_8\text{O}_3\text{Fe}_2\text{I}_2\text{SiU}$  requires: C, 40.93; H, 4.00; N, 7.79 %. Magnetic moment (SQUID, 300 K):  $\mu_{\text{eff}}$  7.74  $\mu_{\text{B}}$ ; MS(ES):  $m/z$  343 (37.7 %,  $[\text{UO}(\text{OSi}(\text{CH}_3)_3)]^+$ ).

**Alternative syntheses of **3** – A.** To a stirred mixture of **1** (0.1 g, 0.09 mmol) and KH (9 mg, 0.23 mmol) was added thf (20 mL) at -78 °C, and the mixture allowed to warm to room temperature over 45 min. The resulting mixture was filtered dropwise on to a stirred slurry of  $\text{FeI}_2$  (56 mg, 0.18 mmol) and  $\text{N}(\text{SiMe}_3)_3$  (21 mg, 0.09 mmol) in thf (10 mL, -78 °C). Room temperature work up yielded 0.09 g, 69 % of **3** as a dark red solid. **B.** To a stirred mixture of **1** (0.10 g, 0.09 mmol) and KH (9 mg, 0.23 mmol) was added thf (20 mL) at -78 °C, and the mixture allowed to warm to room temperature over 45 min. The resulting mixture was filtered



dropwise on to a stirred slurry of  $\text{FeI}_2$  (56 mg, 0.18 mmol) and  $\text{PhCH}_2\text{SiMe}_3$  (15 mg, 0.09 mmol) in thf (15 mL,  $-78^\circ\text{C}$ ). Room temperature work up yielded 0.109 g, 85 % of **3** as a dark red solid.

**[UO(OSiMe<sub>3</sub>)(thf)Zn<sub>2</sub>I<sub>2</sub>(L)], 5** – To a stirred mixture of **1** (0.34 g, 0.32 mmol) and  $\text{KN}(\text{SiMe}_3)_2$  (0.13 g, 0.63 mmol) was added thf (20 mL) at  $-78^\circ\text{C}$ . After 15 min, the mixture was added dropwise to a stirred slurry of  $\text{ZnI}_2$  (0.20 g, 0.63 mmol) in toluene (20 mL,  $-78^\circ\text{C}$ ). Room temperature work up yielded 0.21 g, 46 % of **5** as a pale brown solid. **Analysis.** Found: C, 40.30; H, 3.91; 7.70.  $\text{C}_{49}\text{H}_{57}\text{N}_8\text{I}_2\text{O}_3\text{SiZn}_2\text{U}$  requires: C, 40.40; H, 3.95; N, 7.69 %. Magnetic moment (SQUID, 300 K):  $\mu_{\text{eff}}$  2.38  $\mu_{\text{B}}$ . EPR, frozen glass methyl-thf solution (5K, 0-1.6T, 2mW, Freq. 9.610794 GHz),  $g = 2.2$ .

**[UO(OSiMe<sub>3</sub>)(thf)Zn<sub>2</sub>Cl<sub>2</sub>(L)], 6** – To a stirred mixture of **1** (0.10 g, 0.09 mmol) and  $\text{KN}(\text{SiMe}_3)_2$  (0.036 g, 0.18 mmol) was added thf (15 mL) at  $-78^\circ\text{C}$ . After 15 min, the mixture was added dropwise to a stirred slurry of  $\text{ZnCl}_2$  (0.025 g, 0.18 mmol) in toluene (20 mL,  $-78^\circ\text{C}$ ). Room temperature work up yielded 0.06 g, 56% of **6** as a pale brown solid. **Analysis.** Found: C, 46.30; H, 4.50; 8.72.  $\text{C}_{49}\text{H}_{57}\text{N}_8\text{Cl}_2\text{O}_3\text{SiZn}_2\text{U}$  requires: C, 46.19; H, 4.52; N, 8.80 %. Magnetic moment (SQUID, 300 K):  $\mu_{\text{eff}}$  3.01  $\mu_{\text{B}}$ .

**Reaction of 1 and  $\text{KN}(\text{SiMe}_3)_2$ : attempted synthesis of [UO(OSiMe<sub>3</sub>)(thf)K<sub>2</sub>L]** – To a stirred mixture of **1** (0.10 g, 0.1 mmol) and  $\text{KN}(\text{SiMe}_3)_2$  (0.041 g, 0.21 mmol) was added thf (20 mL) at  $-78^\circ\text{C}$ . The resulting red solution was allowed to warm to room temperature over 2 hours, after which the volatiles were removed from the now dark brown solution. The solid residues were washed with toluene ( $1 \times 10$  mL), and dried to form a dark brown solid, which was redissolved in a minimal amount of thf (1 – 2 mL) and cooled ( $-30^\circ\text{C}$ ) for 16 hours. The resulting dark precipitate was isolated and was found to be no longer soluble in thf. Analysis indicated that the compound had decomposed.

**Reaction of 1 with cobaltocene and trimethylsilyl triflate: attempted synthesis of**

**[UO(OSiMe<sub>3</sub>)(thf)(H<sub>2</sub>L)] and cobaltocenium triflate** – To a stirred mixture of **1** (0.10 g, 0.09 mmol) and  $\text{Co}(\text{C}_5\text{H}_5)_2$  (0.017 g, 0.09 mmol) was added thf (20 mL) at  $-78^\circ\text{C}$ , and  $\text{Me}_3\text{SiOTf}$  (0.020 g, 0.09 mmol) added into the mixture by syringe. The mixture was allowed to warm to room temperature over 16 hours. The volatiles were removed from the now dark red solution to afford a viscous red oil. Analysis indicated that the compounds had decomposed.

**Reaction of 1 with excess KH; for identification of byproducts** – To cold ( $-35^\circ\text{C}$ ) **1** (10 mg, 0.009 mmol) and KH (2 mg, 0.05 mmol) in a Youngs tap NMR tube was added cold thf (0.5 mL,  $-35^\circ\text{C}$ ) and a few drops of  $\text{C}_6\text{D}_6$ ; upon warming gas evolution was observed. After 10 mins, dissolved dihydrogen was observed in the  $^1\text{H}$  NMR spectrum at  $\delta = 4.4$  ppm.

**Reaction of 1 with 2  $\text{KzN}(\text{SiMe}_3)_2$ ; for identification of byproducts** – To cold ( $-35^\circ\text{C}$ ) **1** (5 mg, 0.005 mmol), and  $\text{KN}(\text{SiMe}_3)_2$  (1.8 mg, 0.009 mmol) in a Youngs tap NMR tube was added cold thf (0.5 mL,  $-35^\circ\text{C}$ ) and a few drops of  $\text{C}_6\text{D}_6$ . After 10 mins, integration of the  $^1\text{H}$  NMR spectral resonances showed that one

molar equivalent of  $\text{HN}(\text{SiMe}_3)_2$  had been formed. No other silylamide-derived byproducts could be identified in the solution.

**Crystallography** – Dark red single crystals of **3** (needle-shaped) and **5** (parallelepiped) were grown from saturated  $\text{C}_6\text{D}_6$  solutions at room temperature.

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